RANEY-NICKEL CATALYSTS PRODUCED BY MECHANICAL ALLOYING

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Abstract. Raney catalysts were prepared by a combination of mechanical alloying and leaching as an alternative in the synthesis of Raney-Nickel catalysts. Binary Al-Ni and ternary Al-Ni-Fe alloys with nominal compositions $Al_{65}Ni_{35}$, $Al_{75}Ni_{25}$, $Al_{65}Ni_{30}Fe_5$, $Al_{75}Ni_{20}Fe_5$ (in atomic percent), were processed from pure elemental powders; they consisted mainly of the intermetallic B2 AlNi phase. Aluminum was selectively removed from the alloys by means of a chemical treatment with hydroxide solutions, resulting in a highly porous solid. Higher Al contents in the alloys produced larger surface area values of the catalysts. Increasing Ni proportion in the final product resulted in higher catalytic activity, while the addition of Fe improved the stability of the catalysts. The Raney-Ni catalysts produced by mechanical alloying and leaching were highly active in the hydrogenation reaction of benzene.

1. INTRODUCTION

Raney-type catalysts were first introduced in 1924; since then, these catalysts, both in powdered and granular form [1], have been widely used in many commercial processes, including hydrogenation of unsaturated organic compounds, such as the catalytic hydrogenation of adiponitrile to hexamethylenediamine, and of benzene to cyclohexane; they have also been used in reductive reactions, as in the alkylation of carbonyl compounds with amines; in the hidrogenolysis of esters and ethers; in fuel cell electrodes and in dehalogenation [2].

Conventional Raney-Ni catalysts are produced by removing aluminum from binary Al-Ni alloys by means of an aqueous alkaline solution. These alloys are prepared by pyrometallurgical (PM) methods [3], generally in the proportion 50:50 wt.%. In the as-cast alloys, a mixture of nickel aluminides

(Al_3Ni, Al_3Ni_2, AlNi) and Al-Al_3Ni eutectic are obtained.

In contrast with conventional methods, Mechanical Alloying (MA) is a process used to produce alloys at room temperature, having a fine microstructure and non-equilibrium phases [4]. It is known as a promising route for the processing of structural intermetallics, superplastic ceramic materials, modified semiconductor materials, protective coatings, and - in general - materials with unusual structure and properties.

Ivanov *et al*. [5] reported that leaching of Al atoms from the B2 structures in mechanically alloyed Ni and Co aluminides led to the formation of metastable bcc Ni and Co phases having a high catalytic activity. However, they did not give details of the leaching treatment, the reductive treatment of their catalysts before test reaction, the experimental conditions during the catalytic reaction, or sur-

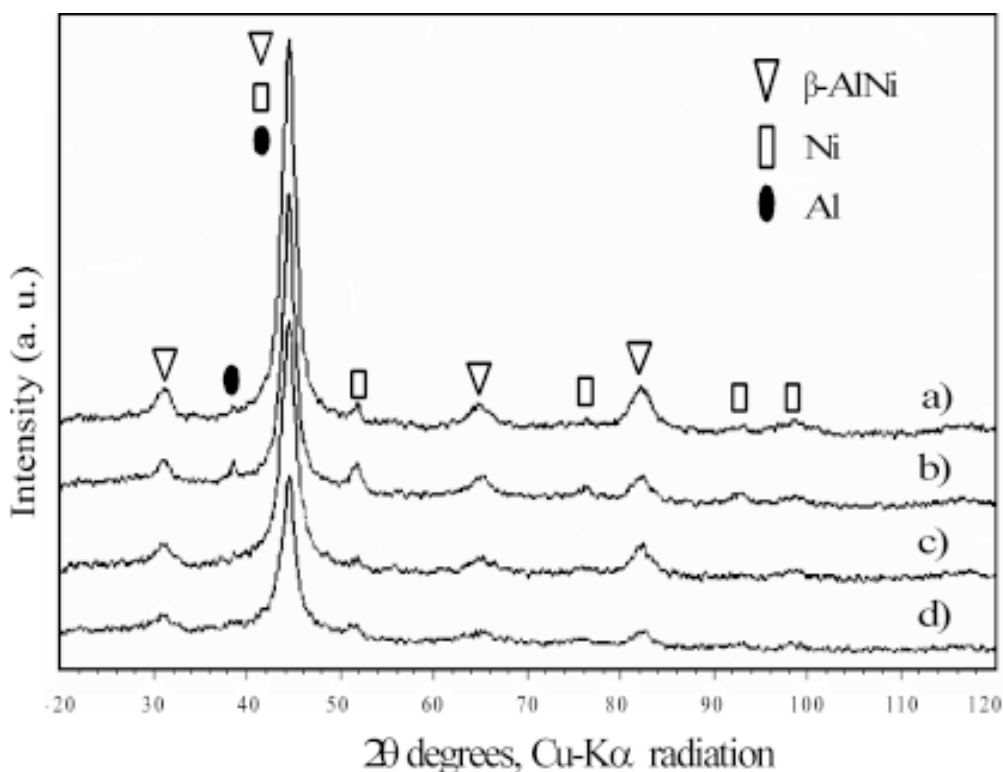Corresponding author: Beatriz Zeifert, e-mail: bzeifert@yahoo.com

Fig. 1. Similarity of the X-ray diffraction patterns of binary and ternary alloys produced by MA. The major phase is B2 AlNi: (a) $Al_{65}Ni_{35}$, (b) $Al_{75}Ni_{25}$, (c) $Al_{65}Ni_{30}Fe_5$, and (d) $Al_{75}Ni_{20}Fe_5$.

face area and porosity in the catalysts. In the present work, MA was applied to obtain metastable Al-Ni and Al-Ni-Fe alloys starting from elemental powder blends [6-10]; from them, by means of a chemical treatment, new skeletal nickel catalysts were produced and evaluated.

2. EXPERIMENTAL PROCEDURE

Elemental Al-Ni (binary alloys) and Al-Ni-Fe (ternary alloys) powder mixtures, with nominal compositions $Al_{65}Ni_{35}$, $Al_{75}Ni_{25}$, $Al_{65}Ni_{30}Fe_5$, $Al_{75}Ni_{20}Fe_5$ (in atomic percent), were milled in an attritor ball mill (Union Process, model 1-S), equipped with a water cooled jacket and a stainless steel vessel container of 3.81 l capacity. Stainless steel balls (3.2 mm diameter) were used as milling media. The attritor was operated for 120 hours at 350 RPM under a continuous flow of argon gas. The powder charge was 100 g and the ball-to-powder weight ratio was 30:1. A volume of 20 ml of methanol was used as a process control agent.

In order to prevent the mechanically alloyed product from spontaneous igniting on removal from the attritor, the flow of argon gas was stopped at the end of each run and, before opening the reactor, atmospheric air was allowed to enter into the vessel, while the attritor was set to rotate at a reduced speed (70 RPM) for about 8 hours.

The as-milled powder samples were then treated with a 20% KOH aqueous solution, held at its boiling point (digestion) for 2 hours, in order to selectively leach away the aluminum atoms. This reaction led to the removal of the major portion of the aluminum in the alloys and the production of the MA Raney-Nickel catalysts. The leached materials were also pyrophoric, but they could be passivated by the formation of a protective oxidation film in a controlled mixture of argon and oxygen.

The chemical composition of the materials was determined by Energy-Dispersive X-ray Spectrometry (EDS). The materials were also characterized by X-ray Diffraction (XRD), using Cu-K_α radiation, Scanning and Transmission Electron Microscopy
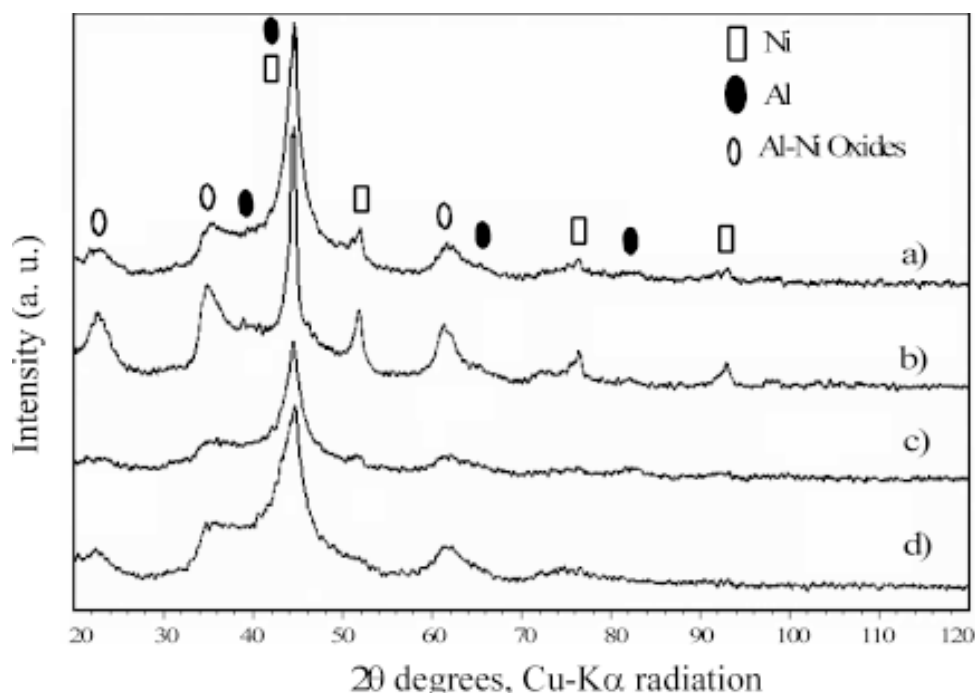
Fig. 2. X-ray diffraction patterns of the MA Raney-Ni catalysts: (a) $Al_{65}Ni_{35}$ leached, (b) $Al_{75}Ni_{25}$ leached, (c) $Al_{65}Ni_{30}Fe_5$ leached, and (d) $Al_{75}Ni_{20}Fe_5$ leached.

(SEM and TEM) and measurements of Specific Surface Area and Porosity by nitrogen physisorption (BET).

Measurements of catalytic activity of leached MA binary and ternary alloys and a commercial Raney-Ni were carried out employing the benzene hydrogenation reaction in a conventional, continuous flow microreactor system with fixed bed. The activation of the catalysts was made *in situ* by a treatment with hydrogen at 773K for 3 hours. The catalytic evaluation was performed in the vapor phase, at atmospheric pressure and a reaction temperature of 323K. Samples of 0.04 g of catalysts were used and benzene was fed by saturation at 24.7 mm Hg partial pressure with 15.8 l/h of hydrogen gas flow. The degree of conversion of benzene to cyclohexane was first measured after 15 min of stabilization of the reactor effluent, and a gas chromatograph system was used to determine the composition of the products. The conversion of benzene (X_A) is defined as the fraction of benzene converted to all products. The selectivity to cyclohexane is defined as the amount of benzene converted to cyclohexane divided by the amount

of reactant converted to all products, reported as mole percentage.

3. RESULTS AND DISCUSSION

3.1. Crystallographic structure

The as-milled binary and ternary mixtures produced similar diffraction patterns, shown in Fig. 1.

Even though the mixture compositions were out of the range in which the B2 AlNi phase exists in equilibrium conditions, this phase was the major phase in all cases. Iron from the ternary alloys was not detected in the diffraction patterns, neither modified the nature of the existing phases with respect to the binary systems. The width of the diffraction peaks in Fig. 1 suggests that the crystallite size in the particles is very small, as expected from the MA process.

After leaching of Al, the crystalline structure of these materials changed from B2 AlNi to Ni fcc in both binary and ternary alloys, as shown in Fig. 2. The XRD patterns of the MA catalysts had additional lines due to the presence of oxide compounds. These results differ from those of Ivanov

Table 1. Composition of MA alloys, MA leached alloys and commercial catalyst (at.%).

Nominal Mixture Composition	EDS Alloy Composition	EDS Leached Alloy Composition
$Al_{65}Ni_{35}$	$Al_{56}Ni_{44}$	$Al_{14}Ni_{86}$
$Al_{75}Ni_{25}$	$Al_{70}Ni_{30}$	$Al_{17}Ni_{83}$
$Al_{65}Ni_{30}Fe_5$	$Al_{63}Ni_{27}Fe_{10}$	$Al_{17}Ni_{71}Fe_{12}$
$Al_{75}Ni_{20}Fe_5$	$Al_{70}Ni_{24}Fe_6$	$Al_{12}Ni_{70}Fe_{18}$
$Al_{69}Ni_{31}$	Commercial Raney-Ni	$Al_{17}Ni_{83}$

Table 2. Results of BET determinations of the MA and PM catalysts.

Sample	Surface area (m^2/g)	Pore Volume (cm^3/g)	Mean Pore Diameter (Å)
$Al_{65}Ni_{35}$ leached	139	0.095	27
$Al_{65}Ni_{30}Fe_5$ leached	146	0.094	26
$Al_{75}Ni_{25}$ leached	247	0.227	37
$Al_{75}Ni_{20}Fe_5$ leached	273	0.232	34
Commercial Raney-Ni	53	0.076	55
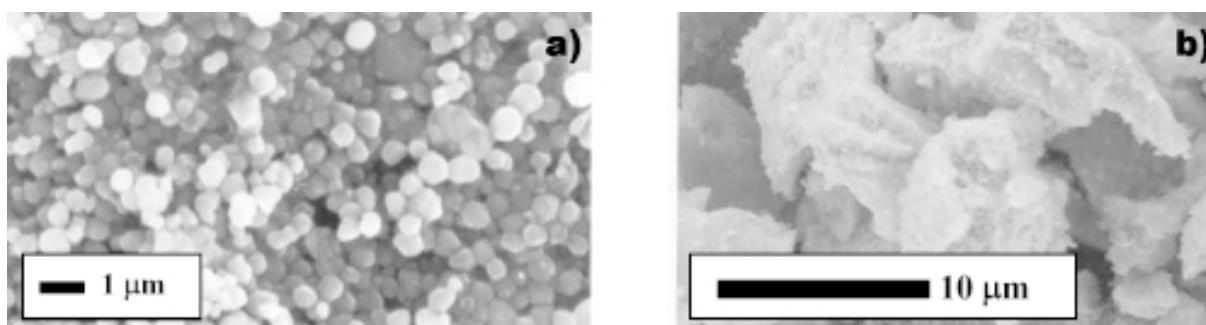
Fig. 3. SEM of (a) MA Raney Nickel and (b) Conventional Raney Nickel catalysts.

et al. [5] in the sense that their leaching did not induce a significant change in the diffraction pattern of the as-milled powders, even though 60-70% of Al atoms were said to be removed in the work of these authors. The addition of 5 at.% Fe, in substitution of Ni, was expected to make the metastable bcc structure of Ni less unstable after the leaching treatment. However, the transition of B2 to fcc structure took place even with the addition of Fe and the use of "softer" leaching conditions (5 wt% KOH, without digestion treatment).

3.2. Composition

The mean compositions of the alloys, before and after leaching, as well as that of the commercial Raney-Ni are indicated in Table 1.

Microanalysis of the as-milled powders indicated Al losses with respect to the nominal composition of the powder mixtures, as well as no evidence of iron contamination from wear of the milling device. The facility to remove aluminum atoms from the alloys or the quantity of residual aluminum, under the same leaching conditions, did not depend on
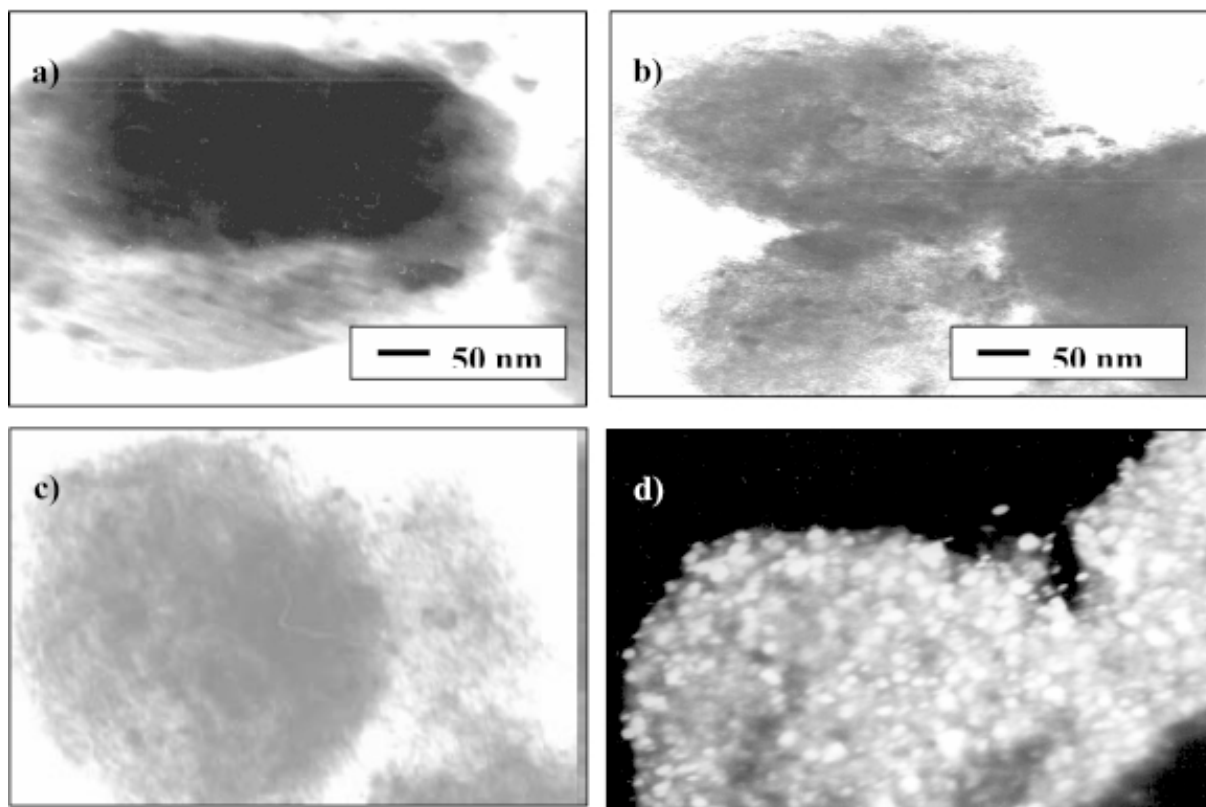
Fig. 4. TEM of (a) MA $Al_{75}Ni_{25}$ alloy and (b), (c), (d) $Al_{75}Ni_{25}$ leached alloy (catalyst).

the presence of Fe. According to the results in Table 1, more than 70% of the original quantity of Al atoms was removed by the alkaline solution.

3.3. Particle size of Raney-Ni catalysts

Observations by SEM identified the MA Raney-Ni catalysts as sponge-like agglomerates of nearly spherical particles of individual sizes ranging from 0.1 to 3 mm. The commercial Raney-Ni catalyst showed angular and irregular particles with sizes between 3 and 30 mm, as shown in Fig. 3.

3.4. Specific surface area and porosity

Table 2 presents the average values of surface area, and of volume and diameter of pores derived from BET measurements. The values of surface area for MA Raney-Ni catalysts are considerably greater (>200%) than those from commercial Raney-Ni. Values of pore diameter and volume of

pores in the MA catalysts are significantly smaller and larger, respectively, compared to those found in the commercial catalyst.

The Al content in the MA alloys had a direct influence over the surface area values of the catalysts: higher the nominal aluminum content, larger the surface areas obtained.

Fig. 4 displays TEM micrographs corresponding to the $Al_{75}Ni_{25}$ alloy and the $Al_{75}Ni_{25}$ leached alloy, where it is possible to see how the powder particles were modified by the alkaline chemical treatment, to produce a porous catalyst with a large specific surface area. The leached sample has a fine fibrous structure in contrast with the same sample without leaching, which shows a compact form [11].

3.5. Catalytic properties

The catalytic activity of the materials produced by MA was compared in the benzene hydrogenation reaction with that of the commercial catalyst under
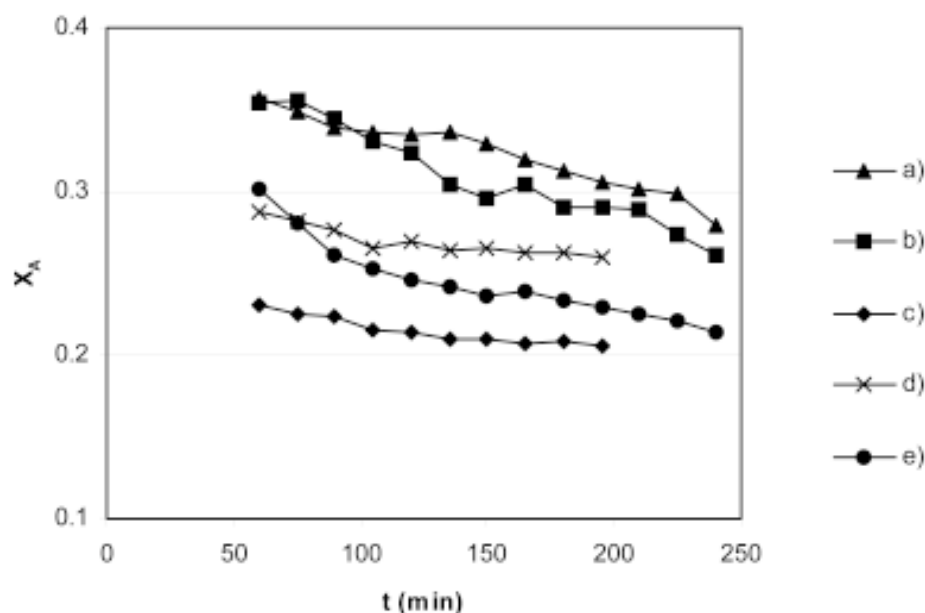
Fig. 5. Comparison of the MA Raney catalysts with the commercial one in the benzene conversion (X_A) to cyclohexane at 50 °C as a function of time. (a) leached $Al_{65}Ni_{35}$, (b) leached $Al_{75}Ni_{25}$, (c) leached $Al_{65}Ni_{30}Fe_5$, (d) leached $Al_{75}Ni_{20}Fe_5$, and (e) commercial Raney-Ni.

the same conditions. Typical results are shown in Fig. 5.

The Raney-Ni catalysts prepared by MA had a better performance than the commercial catalyst. All of them were selective to cyclohexane. In the tests reported in Fig. 5, the binary leached alloys showed the highest conversions, followed by a ternary alloy and the commercial Raney-Ni. It is important to consider the differences in Ni concentration among these catalysts, as shown in Table I. Higher Ni proportions in the MA catalysts clearly had a favorable effect on the conversion of benzene to cyclohexane, indicating that Ni is the active phase of the catalyst.

Both MA catalysts derived from ternary alloys had similar Ni content, but the most active one was that with the larger surface area. The addition of Fe did not increase the conversion of benzene, as compared to the binary Al-Ni alloys, but it improved the catalytic stability as shown by the flat slope of the plots in Fig. 5.

These results indicate that high Ni contents in the catalysts, large surface areas (high Al contents in the precursor alloys), and addition of Fe are some of the factors to consider in further development of these catalysts.

4. CONCLUSIONS

Raney-Ni catalysts produced from mechanically alloyed powders had some special characteristics. Both binary and ternary precursor alloys were constituted mainly by a metastable, nanocrystalline B2 AlNi phase. The most important effect of mechanical alloying was the reduction of particles size, and as consequently, a substantial increasing in surface areas values.

The combination of mechanical alloying and chemical leaching allowed the production of highly porous solids with surface areas larger (more than 5 times) than the ones obtained in conventional Raney-Ni catalysts. The powder particles acquired a very fine fibrous structure as a result of the alkaline treatment. The Al content in the MA alloys had a direct influence on the surface area values of the catalysts: the higher the nominal aluminum content, the larger the surface areas obtained.

The MA catalysts derived from binary alloys were the most active of all. Higher Ni proportions in the MA catalysts had a favorable effect on the conversion of benzene to cyclohexane.

Addition of Fe did not improve the conversion of benzene, as compared to the binary Al-Ni alloys, but it did improve the stability of the catalysts.

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